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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003901559 for a patent by UNISEARCH LIMITED as filed on 07 April 2003.

WITNESS my hand this
Thirtieth day of March 2004

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AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION

Invention Title: **Glass texturing method**

The invention is described in the following statement:

Glass texturing method

Field of the invention

The present invention relates broadly to a method of texturing a glass surface, to a method of manufacturing a photovoltaic device, to a textured glass surface, and to a photovoltaic device.

Background of the invention

Textured glass surfaces are useful for a number of applications, including photovoltaic devices or applications in which it is desired to scatter light rays such that objects are no longer clearly visible through the glass.

In photovoltaic devices, light trapping is used to trap light in the active region of the device. The more light is trapped in the device the higher the light-generated photocurrent, and consequently the higher the energy conversion efficiency of the device. Therefore, light trapping is an important issue when trying to improve the conversion efficiency of photovoltaic devices and is particularly important in thin-film devices. Because most photovoltaic devices involve a glass pane, light trapping in these devices can be realised by texturing the glass pane.

Conventionally, chemical texturing or sand blasting are used for texturing glass panes. Furthermore, alternative approaches have recently been disclosed for preparing textured glass surfaces. One of those approaches uses metal crystal deposits on a glass surface to form very fine crystals and thereby producing the glass texture effect. Another approach uses a liquid surface coating ("sol-gel") containing SiO₂ spheres that, after densification, produces a textured glass surface.

However, these methods have specific disadvantages for photovoltaic device applications. Chemical texturing and sand blasting both cause cracks and non-uniform feature size on the glass surface, which can adversely affect photovoltaic device fabrication and/or performance (for instance by causing electrical shunts in the devices). On the other hand, the use of fine metal crystals for making a textured glass surface appears to be quite an expensive method. Finally, it appears to be difficult to scale up the sol-gel method to very large dimensions (~ 1 m²) as required for photovoltaic panels.

In at least preferred embodiments, the present invention seeks to provide an alternative method of texturing a glass surface which addresses one or more of these disadvantages.

Summary of the invention

In accordance with a first aspect of the present invention there is provided a method of 5 texturing a glass surface, the method comprising the steps of coating the glass surface with a material film, stimulating a reaction at the interface between the glass and the material film resulting in the formation of reaction products at the interface, and removing the material film and the reaction products from the glass surface.

In one embodiment, the step of stimulating the reaction at the interface comprises 10 thermal annealing. The thermal annealing may be conducted in a controlled ambient atmosphere.

The material film may comprise a single material or compound material.

The glass surface preferably is initially substantially flat.

The material film in one embodiment comprises aluminium. The reaction products may 15 comprise aluminium oxide.

The step of removing the material film and the reaction products may comprise one or more etching steps. The etching steps may comprise a chemical etch.

The glass may comprise quartz, float glass, or non-float glass.

In accordance with a second aspect of the present invention there is provided a method 20 of manufacturing a photovoltaic device, the method comprises the steps of texturing a glass surface utilising a method as defined in the first aspect, and depositing a semiconductor film on the textured glass surface, whereby the glass-facing surface of the semiconductor film exhibits substantially the same degree of texture as the glass surface.

Preferably, the semiconductor film is deposited in a manner such that substantially no 25 gaps or voids exist between the textured glass surface and the semiconductor film.

The method may further comprise forming a dielectric barrier layer between the glass and the semiconductor. Preferably, the dielectric layer is formed on the textured glass surface prior to the deposition of the semiconductor film. The dielectric barrier layer may comprise silicon oxide or silicon nitride.

The semiconductor film may comprise a crystalline and/or an amorphous semiconductor material. The semiconductor material may comprise silicon.

In accordance with a third aspect of the present invention there is provided a textured glass surface formed utilising a method as defined in the first aspect.

- 5 In accordance with a fourth aspect of the present invention there is provided a photovoltaic device manufactured utilising a method as defined in the second aspect.

Brief description of the drawings

Preferred embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings in which:

- 10 Figures 1 to 4 are schematic drawings illustrating a method of texturing the surface of a glass pane, embodying the present invention.

Figure 5 shows a FIB (focused ion beam) microscopical photograph of the top surface of a silicon-coated textured glass pane, embodying the present invention.

- 15 Figure 6 shows a FIB microscopical photograph of a different region of the sample of Figure 5.

Figure 7 shows the measured light trapping properties of the sample of Figure 5, compared with prior art samples.

Detailed description of the embodiments

- 20 The preferred embodiment described provides a method of texturing a glass surface suitable for use in the manufacturing of a thin-film semiconductor photovoltaic device.

Figures 1 to 4 are schematic drawings illustrating a method of texturing the surface of a glass pane 10, embodying the present invention.

In a first step shown in Figure 2, the glass pane 10 is coated with an aluminium film 11, utilising, in the example embodiment, thermal high-vacuum evaporation at about 10^{-5} Torr.

- 25 Next, the Al-coated glass pane (see Figure 2) is thermally annealed at elevated temperature, in the example embodiment in a two-step process with 120mins at 500°C, followed by 120mins at 620°C in a nitrogen atmosphere. In the example embodiment, the initial aluminium coating 11 is of a thickness of about 500nm.

It has been found by the applicants that the Al reacts spatially non-uniformly with the glass pane, forming mixtures (12 in Figure 3) of Al_2O_3 and silicon. A subsequent removal of both the Al film 11 and the reaction products 12 forms a textured glass surface as schematically shown in Figure 4. In the example embodiment, a 2-step chemical etch (10mins in phosphoric acid at 110°C, followed by 30 secs in a 1:1HF/HNO₃ solution at room temperature) was used to remove the reaction products 12 and aluminium film 11. It is noted here, that, depending on the type of removal technique, for example the type of etching solution, used, some amount of glass that has not reacted with the coating can also be removed, if desired.

The dimples (13 in Figure 4) in the glass pane result from the removal of the Al/glass reaction products 12. The average size of the dimples can be adjusted over a wide range (from less than 1 μm to up to 10 μm) by e.g. selecting a suitable thermal annealing profile and/or a suitable removal technique for the Al/glass reaction products 12. This dimple size is well suited for thin-film photovoltaic applications because in those devices the semiconductor film thickness is typically in the range 0.5 - 3 μm .

In the preferred embodiment, the method textures the glass in such a way that there are no "overhanging" regions (i.e. if the textured glass pane of Fig. 4 were illuminated by parallel light from above, there were no shaded regions within the dimples of the surface texture). This feature is advantageous for device applications, for instance if the subsequently formed semiconductor film everywhere needs to be in intimate contact with the glass (i.e., there must be no voids or gaps between the glass and the semiconductor film).

Another advantageous feature of textured glass samples embodying the present invention is that their transmission for light is only very weakly reduced by the texture.

Figure 5 shows a FIB microscopical photograph of the top surface of a silicon-coated textured glass pane fabricated in accordance with the described embodiment. The silicon film 50 is of polycrystalline nature and has a thickness of about 1.5 μm (i.e., similar to the dimensions of the texture features). It was created by thermal annealing ("solid-phase crystallisation") of a plasma enhanced chemical vapour deposition (PECVD)-deposited amorphous silicon film. The striking feature of the silicon film 50 is its cauliflower-like nature, caused by the textured glass surface [note that the silicon film has a planar, smooth top surface if fabricated on a non-textured (i.e., planar) glass pane]. The cauliflower-like top surface of the silicon film is an indicator for good light trapping characteristics.

Figure 6 shows a FIB microscopical photograph of a different region of the same sample, whereby additionally a trench was milled (using gallium ions) into the sample surface to reveal the cross-sectional properties of both the textured glass pane 52 and the polycrystalline silicon film 50 subsequently formed on the textured glass surface 52. The lateral marker in Fig. 5 represents 2 μm . It can be seen that the poly-Si film 50 is everywhere in intimate contact with the textured glass surface and that there are no voids or gaps between the glass 52 and the silicon film 50. This is advantageous for many device applications due to issues such as adhesion of the semiconductor film to the glass, long-term stability of the device, etc..

Another feature visible in Figure 6, advantageous for good light trapping in thin-film 10 photovoltaic devices, is the fact that in most regions of the sample the two surfaces of the semiconductor film 50 are sufficiently non-parallel, leading to the trapping of light due to the phenomenon of total internal reflection. However, it is noted that even if the two surfaces are substantially parallel, i.e if the texture of the glass-facing surface of the semiconductor film 50 is "directly transferred", resulting in a corresponding texture on the surface facing away from 15 the glass 52, useful light trapping characteristics can still be achieved.

The light trapping can be further improved in actual devices by incorporating a back-surface reflector (BSR) (not shown) for near-infrared photons. The BSR can, for instance, be a silver or aluminium film. The BSR is either deposited onto the semiconductor film 50 (if the sunlight enters the semiconductor through the glass) or onto the non-textured glass surface (if 20 the semiconductor-coated, textured side of the glass faces the sun).

Figure 7 shows that excellent light trapping is realised in thin (~1.5 micron) 25 polycrystalline silicon films formed on glass panes textured according to the described embodiment. The curve 70 labelled "Al-textured glass" was measured on the sample of Figure 5. The plotted parameter is the measured internal absorption efficiency (IAE) which, for each wavelength, describes which fraction of those photons that entered the Si film is absorbed within the Si film. The higher the IAE the better the light trapping.

Also shown, for comparison, is the measured IAE of a 1.5- μm thick poly-Si film on a planar glass pane (curve 74) and on a sandblasted glass pane (curve 72). Clearly, the Al-textured glass provides by far the best light trapping of the three investigated structures. Note that the 30 samples did not have a back surface reflector (BSR) during these optical measurements and

hence the IAE of actual devices (such as thin-film photovoltaics) can be further improved by adding a suitable BSR.

It is further noted that glass panes textured in accordance with the described embodiment efficiently scatter light rays that pass through the glass panes, making them useful for other applications outside their use for photovoltaic devices. One such application is e.g. as glass panes for scattering windows or screens.

It will be appreciated by the person skilled in the art that numerous modifications and/or variations may be made to the present invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present 10 embodiments are, therefore, to be considered in all respects to be illustrative and not restrictive.

In the claims that follow and in the summary of the invention, except where the context requires otherwise due to express language or necessary implication the word "comprising" is used in the sense of "including", i.e. the features specified may be associated with further features in various embodiments of the invention.

Claims

1. A method of texturing a glass surface, the method comprising the steps of:
 - coating the glass surface with a material film,
 - stimulating a reaction at the interface between the glass and the material film resulting in the formation of reaction products at the interface, and
 - removing the material film and the reaction products from the glass surface.
2. A method as claimed in claim 1, wherein the step of stimulating the reaction at the interface comprises thermal annealing.
3. A method as claimed in claim 2, wherein the thermal annealing is conducted in a controlled ambient atmosphere.
4. A method as claimed in any one of the preceding claims, wherein the material film comprises a single material or compound material.
5. A method as claimed in any one of the preceding claims, wherein the glass surface is initially substantially flat.
- 15 6. A method as claimed in any one of the preceding claims, wherein the material film comprises aluminium.
7. A method as claimed in claim 6, wherein the reaction products comprise aluminium oxide and/or silicon.
- 20 8. A method as claimed in any one of the preceding claims, wherein the step of removing the material film and the reaction products comprises one or more etching steps.
9. A method as claimed in claim 8, wherein the etching steps comprise a chemical etch.
10. A method as claimed in any one of the preceding claims, wherein the glass comprises quartz, float glass, or non-float glass.
- 25 11. A method of manufacturing a photovoltaic device, the method comprises the steps of texturing a glass surface utilising a method as claimed in any one of the preceding claims, and depositing a semiconductor film on the textured glass surface, whereby the glass-

facing surface of the semiconductor film exhibits substantially the same degree of texture as the glass surface.

12. A method as claimed in claim 11, wherein the semiconductor film is deposited in a manner such that substantially no gaps or voids exist between the textured glass surface and the semiconductor film.

5 13. A method as claimed in any one of claims 11 or 12, wherein the method further comprises forming a dielectric barrier layer between the glass and the semiconductor.

14. A method as claimed in claim 13, wherein the dielectric layer is formed on the textured glass surface prior to the deposition of the semiconductor film.

10 15. A method as claimed in claims 13 or 14, wherein the barrier layer comprises silicon oxide or silicon nitride.

16. A method as claimed in any one of claims 11 to 15, wherein the semiconductor film comprises a crystalline and/or an amorphous semiconductor material.

15 17. A method as claimed in claim 16, wherein the semiconductor material comprises silicon.

18. A textured glass surface formed utilising a method as claimed in any one of claims 1 to 10.

19. A photovoltaic device manufactured utilising a method as claimed in any one of claims 11 to 17.

20 20. A method of texturing a glass surface, substantially as herein described with reference to the accompanying drawings.

21. A method of manufacturing a photovoltaic device, substantially as herein described with reference to the accompanying drawings.

25 22. A textured glass surface, substantially as herein described with reference to the accompanying drawings.

23. A photovoltaic device, substantially as herein described with reference to the accompanying drawings.

Dated this 7th day of April 2003

**Unisearch Limited
by its attorneys
Freehills Carter Smith Beadle**



Figure 1

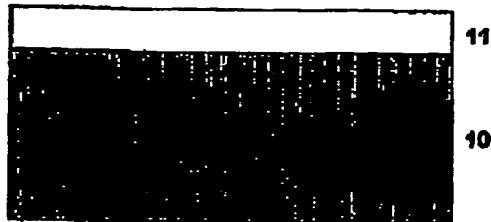


Figure 2

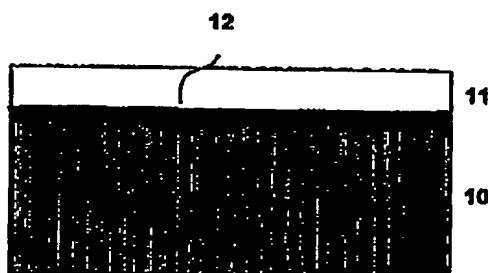


Figure 3

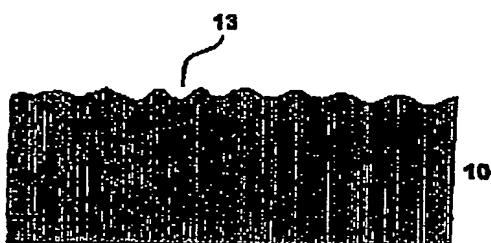
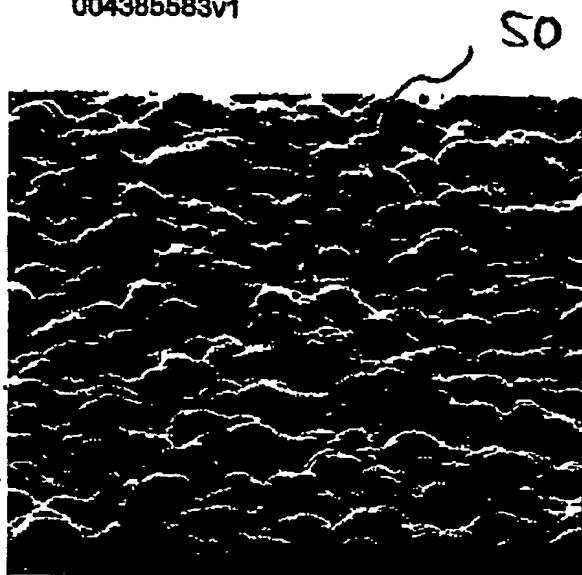
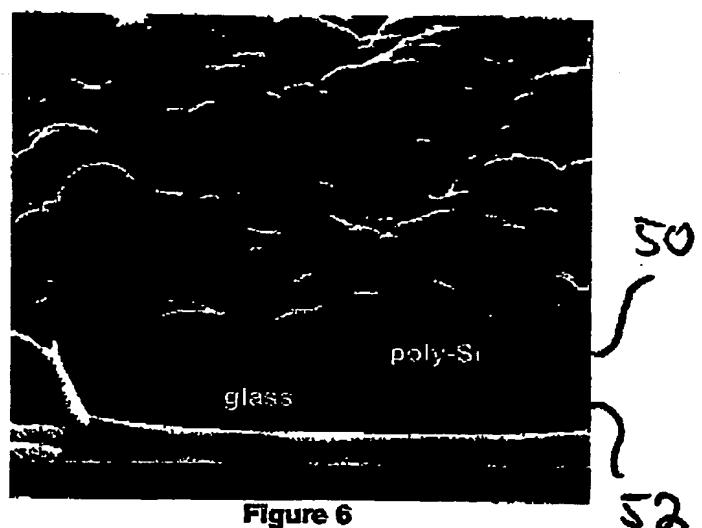
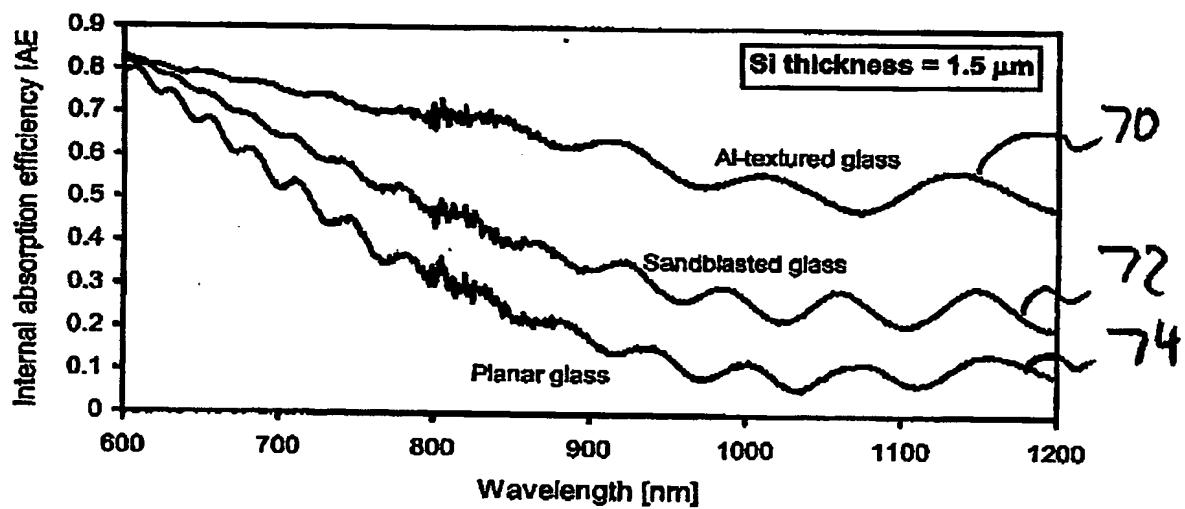


Figure 4

**Figure 5****Figure 6****Figure 7**